

Some Problems of the Electrical Double Layer

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Introduction

Detailed results for the adsorption of ions at mercury electrodes are now available for a number of different systems. Results for the potassium halides in water are summarized elsewhere.¹ Li,² Rb,² and Cs^{2,3} chlorides have also been studied in water. Surface excesses at the mercury-water interphase have also been obtained for NaCNS,^{2,4} NaCN,² NaClO₄,² NH₄ClO₄ in NH₄F,⁵ HClO₄,⁶ NaNO₃,⁷ NH₄NO₃ in NH₄F,⁸ NaClO₃,² NaBrO₃,² NaN₃,⁹ NaH₂PO₄,¹⁰ TlF,¹¹ TlNO₃,¹² sodium p-toluene sulphonate,¹³ sodium benzene-m-disulphonate,¹⁴ sodium formate,¹⁵ sodium acetate,¹⁵ sodium propionate,¹⁵ concentrated solutions of strong acids,¹⁶ tetra-alkyl ammonium iodides,¹⁷ long chain ions,¹⁸ and aromatic cations.^{19,20,21} The adsorption of ions on mercury from non-aqueous solution has been studied to a smaller extent but results are available for KI in KF in methanol,²² KCl,²³ NaCl,²⁴ CsCl,²⁴ and KI²⁵ in formamide, LiCl, KCl, and CsCl in N-methyl formamide, alkali formates, phosphates, and sulphates in formic acid.¹⁵ The adsorption of thiourea has been studied in detail also in water,²⁷ methanol,²² and formamide.²⁸ The adsorption of other non-electrolytes has been reviewed thoroughly by Damaskin and Frumkin.²⁹ Adsorption on solid metals has also been studied in a more quantitative way in recent years.³⁰ Although the results are of considerable interest, they are in general not sufficiently accurate to be useful in the examination of the detailed structure of the double layer.

The Diffuse Layer

The adsorption of ions at an electrode is usefully classified as specific or non-specific. This is an operational classification which in practice depends on the simple model of non-specific adsorption introduced by Gouy³¹ and Chapman.³² This model is analogous to the Debye-Hückel theory of electrolytes. In this model^{33,34,35} adsorption arises as a result of the electrostatic interaction between point charge ions and the charge on the electrode. The size of the ions is introduced only as a distance of closest approach to the electrode (x_2). This results in an ionic atmosphere or diffuse layer extending from x_2 and decaying out into the bulk of the solution, the net charge on this diffuse layer being equal and opposite to that on the metal surface. Specific adsorption is then all adsorption which cannot be accounted for by the Gouy-Chapman theory. Most obviously it will occur when ions can approach the electrode more closely than x_2 and specific 'chemical' interaction occurs between ion and electrode, but other effects, such as the 'squeezing out' of a structure-breaking ion from the bulk of the solution may also contribute to the specific interaction. Because such specific forces are short-range, specifically adsorbed ions are usually located in a monolayer with their centers in a plane at X_1 from the electrode ($x_1 < x_2$).

This is not a very sophisticated model, but as in the case of electrolyte theory, progress beyond the first approximation is difficult. Numerous attempts to improve the theory of the diffuse layer have not resulted in a widely used model for two reasons: first, the theories suggest that modifications are small under practical conditions, and their use is much more complicated than the Gouy-Chapman theory; second, there have been very few experimental tests of the theory under conditions where deviations from it might be expected; i.e., at high concentrations and high electrode charges. Such tests are difficult because under these conditions the diffuse layer makes an insignificant contribution to the electrode capacity. Measurements in mixed electrolytes³⁶ and of the kinetics of electrode reactions^{35,37} provide the most critical tests, but interpretation is not unambiguous. For the limited object of defining specific adsorption, recent theoretical work³⁸ suggests that the relation between cationic and anionic charge contributions in the diffuse

layer is unchanged by improvements in the model; hence, continued use of the Gouy-Chapman theory may be justified. On the other hand, the simple theory probably gives an inaccurate potential distribution in the diffuse layer.

The Inner Layer

The theory of the inner layer is more difficult than that of the diffuse layer because it is a region of very small thickness, probably one solvent molecule thick, and its composition varies within wide limits. It is very doubtful whether macroscopic concepts such as dielectric constant have real meaning for this region although they continue to be used. The problem of electrostatic interaction in the inner layer has been extensively discussed in two recent reviews.^{39,40} As mentioned above, short-range forces between adsorbed particles and between particles and electrode are at least as important in this region as are the electrostatic forces. It seems likely^{14,41} that the two types of forces can be meaningfully separated, at least to a first approximation, in the way first proposed by Stern.³⁹ That is, the non-electrostatic particle-electrode interaction energy is approximately independent of the charge on the electrode. This 'chemical' adsorption energy is clearly⁴⁰ a difference between the energy of interaction of the adsorbing particle with the electrode and that of the solvent particle. A detailed calculation⁴¹ for simple ionic (particularly halide) adsorption has suggested that the observed behavior can be explained without invoking the formation of a chemical bond between the absorbing particle and the electrode. However, it seems more probable that chemical bond formation occurs to a different extent with different species ranging from thiocyanate ion and thiourea where sulphur is undoubtedly bonded to the mercury electrode through to aliphatic sulphonates and carboxylates where bond formation seems very unlikely. Since the two extremes behave in a generally similar way it is unlikely that a very definite conclusion can be made for intermediate cases as to whether bond formation occurs. On the other hand, there seems to be little doubt about the importance of solvation effects⁴⁴ in solution and in the double layer.

The energy of interaction of the adsorbing species with the electrode would be obtained most unambiguously from measurements at very small adsorbed amounts, but these are difficult to make reliably. Consequently, the usual procedure is to use measurements at higher adsorbed densities and to allow for the particle-particle interactions by theoretical calculation or to extrapolate to zero adsorbed density using an adsorption isotherm. This procedure at present introduces uncertainty because accurate calculations of the interaction are not possible and the correct form of the adsorption isotherm is not known, because it depends on a knowledge of the free energy of one component in a dense two-dimensional non-ideal liquid mixture. Nevertheless, an empirical extension^{41, 45, 46} of the Zhukovitskii-Flory-Huggins model seems to satisfy a number of limiting criteria and to be capable of useful interpretation: allowance for difference of size of adsorbate and solvent, approach to saturation, etc. At sufficiently low densities the interaction coefficient may be simply related to a two-dimensional second virial coefficient. In a number of ionic systems this is found to be extremely large, possibly reflecting the strong repulsive forces between ions of like sign. However, these forces are to a large extent screened³⁴ by the presence of conducting walls (metal and diffuse layer) on either side of the inner layer. Further, the magnitude of the second virial coefficient of iodide ion is strongly solvent dependent.^{22,25} This does not seem to be readily explicable in simple electrostatic terms since the effective dielectric constant in the inner layer should vary very little with the solvent. In contrast, the second virial coefficient of thiourea has almost the same value in the three solvents studied^{22,27,28} and this value is about that to be expected from a simple electrostatic model.⁴⁷ It is possible that the behavior of ions is due to solvation in the inner layer.⁸

The problem of solvent properties in the inner layer has been frequently related to the appearance of a 'hump' in the capacity-potential curve.⁴⁸ On the other hand, the 'hump' has been attributed entirely to the result of ionic specific adsorption.⁴³ There is no doubt that the latter can cause humps; in the simplest case the capacity is proportional to the slope of the adsorption isotherm which must pass through a maximum between zero coverage and saturation; the benzene-disulphonate

ion¹⁴ is a good illustration of such behavior. Nevertheless, there is little doubt that the hump in formamide⁴⁹ and in N-methylformamide⁵⁰ is attributable to solvent reorientation and it is probable that this effect is also present in water. Until recently it seemed that humps were absent in solvents of lower dielectric constant than water. Now, however, it is known that they also occur in propylene carbonate,⁵¹ ethylene carbonate,⁵² dimethyl sulphoxide,⁵³ sulpholane,⁵¹ 4-butylolactone,⁵² and 4-valerolactone.⁵² However, the nature of the hump in these solvents remains to be investigated. The simultaneous presence of an adsorption hump and a solvent hump can be discerned in the capacity curve of thiourea in a formamide solution of KF (Fig. 1). It has also been suggested⁵⁴ that the presence of adsorbed ions may enhance or reduce a hump due to solvent reorientation by interacting with the solvent molecules in the inner layer. Some support for this view may be obtained from a consideration of the isoelectronic series: ClO_4^- , HSO_4^- , and H_2PO_4^- . These ions are all about the same size but their interaction with bulk water varies considerably:⁵⁵ ClO_4^- is a structure breaker while H_2PO_4^- is heavily hydrated. This sequence is reflected in their adsorption behavior on mercury. At potentials negative to the point of zero charge the amount of adsorption is in the sequence $\text{ClO}_4^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^-$ while at high positive charges the sequence is reversed. The magnitude of the hump is also in the sequence $\text{ClO}_4^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^-$ (Fig. 2). It is possible that the presence of ClO_4^- in the inner layer facilitates the reorientation of water, while the HPO_4^- ion tends to reduce its freedom to reorient.

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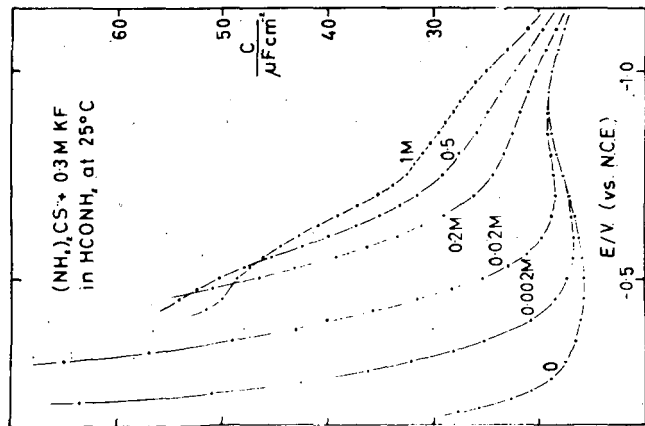


Fig. 1

Capacity of a mercury electrode as a function of potential. The 0.3 M potassium fluoride solution in anhydrous formamide contained thiourea at the concentration shown by each line.

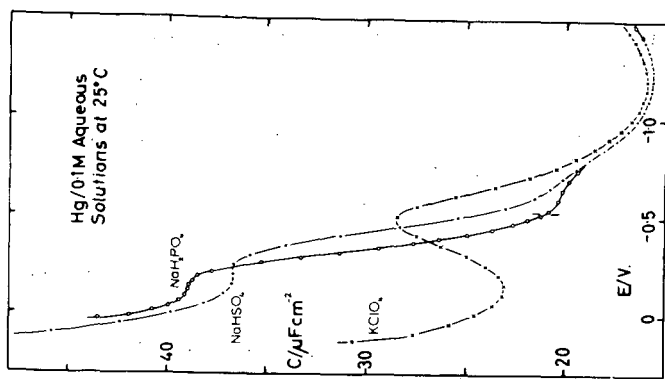


Fig. 2

Capacity of a mercury electrode as a function of potential for 0.1 M aqueous solutions of potassium perchlorate, sodium bisulphate and sodium dihydrogen phosphate.